

**Observation of biogenic secondary organic aerosols in the
atmosphere of a mountain site in central China:
Temperature and relative humidity effects**

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Abstract: Secondary organic aerosols (SOA) derived from isoprene, pinene and caryophyllene were determined for PM₁₀ and size-segregated (9-stages) aerosols collected at the summit (2060 m, a.s.l.) of Mt. Hua, central China during the summer of 2009. Concentrations of estimated isoprene, α -/ β -pinene and β -caryophyllene derived secondary organic carbon (SOC) are 81 ± 53 , 29 ± 14 and 98 ± 53 ng m⁻³, accounting for $2.7 \pm 1.0\%$, $0.8 \pm 0.2\%$ and $2.1 \pm 1.0\%$ of OC, respectively. Concentrations of biogenic (BSOA, the isoprene/pinene/caryophyllene oxidation products) and anthropogenic (ASOA, mainly aromatic acids) SOA positively correlated with temperature ($R=0.57-0.90$). However, a decreasing trend of BSOA concentration with an increase in relative humidity (RH) was observed during the sampling period, although a clear trend between ASOA and RH was not found. Based on the AIM Model calculation, we found that during the sampling period an increase in RH resulted in a decrease in the aerosol acidity and thus reduced the effect of acid-catalysis on BSOA formation. Size distribution measurement showed that most of the determined BSOA are formed in aerosol phase and enriched in the fine mode ($<2.1\mu\text{m}$) except for *cis*-pinonic acid, which is formed in gas phase and subsequently partitioned into aerosol phase and thus presents a bimodal pattern with a small peak in the fine mode and a large peak in the coarse mode ($>2.1\mu\text{m}$).

Key words: BSOA; Isoprene, pinene and caryophyllene; Temperature and relative humidity; Size distribution.

1. Introduction

Volatile organic compounds (VOCs) produced from the biosphere have a substantial impact on the atmospheric chemistry. On a global scale, biogenic volatile organic compounds (BVOCs, 1150 Tg yr⁻¹), mostly consisting of isoprene, monoterpenes (such as α -/ β -pinene) and sesquiterpenes (such as β -caryophyllene), are one order of magnitude more abundant than anthropogenic VOCs (Guenther et al., 2006). The high emission of BVOCs can significantly increase the abundance of secondary organic aerosols (SOA) in the atmosphere, which influences the atmospheric radiation budget directly by absorbing and scattering sun light and indirectly by acting as cloud condensation nuclei (CCN) (Kanakidou et al., 2005; Kawamura et al., 2005; Turpin and Huntzicker, 1995). Therefore, numerous studies in the last decade have been devoted to characterizing biogenic secondary organic aerosols (BSOA) in the atmosphere (Kleindienst, 2009; Froyd et al., 2010; Jaoui et al., 2008; Offenberg et al., 2009; Claeys et al., 2004).

China is a large and diverse source of aerosols and trace gases to the atmosphere. Biogenic emission is high in some forested areas of the country. For example, a model study showed that monthly average emission rates of isoprene are more than 30 mg m⁻² day⁻¹ in southeastern, northeastern and central China in summer (Guenther et al., 2006). On the other hand, air pollution in China is serious (Fang et al., 2009; Wang et al., 2006). North China Plain, Guanzhong Basin, and Sichuan Basin in the country are the three most heavily polluted regions in the world, where the annual level of PM_{2.5} on the ground surface was more than 80 μ g m⁻³ during 2001–2006 (van Donkelaar et al., 2010). In the past decade, SOA derived from anthropogenic sources in China has been given much attention. However, BSOA in the country has only been documented by a limited number of studies (Fu et al., 2010; Wang et al., 2008; Ding et al., 2011; Hu et al., 2008) with no report of BSOA for the central part. Atmospheric environment over mountain area is unique because of lower temperature, higher humidity and

stronger solar radiation, and thus chemical and physical properties of mountain aerosols differ from those on lowlands (e.g., urban area). Furthermore, mountain area is a receptor for anthropogenic gas and aerosols originating from lowlands by long-range transport. Thus characterizations of alpine BSOA can improve our understanding on physicochemical properties of aerosols in the atmosphere.

In the current paper, we first investigate molecular composition of BSOA, including those derived from isoprene, pinene and caryophyllene, in airborne particles at the summit (2060 m altitude) of Mt. Hua in central China and their relationship with temperature and relative humidity, and then measure their size distributions to investigate sources and formation mechanisms of BSOA in the alpine atmosphere.

2. Experimental Section

2.1. Sample Collection

Mt. Hua (34°29' N, 110°05'E, 2060 m a.s.l., Fig. 1) is located at the east border of the Qinling Mountain Range in central China, where there are around 3000 species of vegetations. The low-elevation forests of the foothills are dominated by temperate deciduous trees. At the middle elevations, conifers are mixed with broadleaf birch, oak and hornbeam. Fir, cunninghamia, and birch are dominant species of the high-elevation forests (Fu et al., 1996). Collections of PM₁₀ and size-segregated particles were simultaneously performed at the summit of Mt. Hua during the summer of 2009 (July 15~August 25). The samples of July 22–25 and July 27–29 were not collected because of the power interruption. PM₁₀ sample was collected using a medium-volume air sampler (KC-120H, made in China) at an airflow rate of 100 L min⁻¹, while the size-segregated samples were collected using an Andersen 9-stage air sampler (Thermo electronic Company, USA) with the cutoff points of 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4 μm under an airflow rate of 28.3 L min⁻¹. A total of 34 PM₁₀ samples were collected each lasting for 24 hr. The size-resolved aerosols (nine samples per set, three sets in total) were collected for 5–6

days in each set. All samples were collected on pre-baked (450 °C for 8 hr) quartz microfiber filters (Whatman 42). After sampling, the filter was sealed in an aluminum bag and stored at –18 °C prior to analysis. Blank samples (three for PM₁₀ and two sets for size-resolved aerosols) were collected before and after sampling by mounting the filters onto the sampler for about 10 min without sucking any air.

2.2 Sample extraction, derivatization and GC/MS quantification

Detailed methods for extraction, derivatization and gas chromatography/mass spectrometry (GC/MS) analysis were described elsewhere (Wang et al., 2006; Wang et al., 2009a). Briefly, one fourth of the sample/blank filter was cut in pieces and extracted with a mixture of dichloromethane and methanol (2:1, v/v) under ultrasonication (three times and 15 min in each). The extracts were concentrated using a rotary evaporator under a vacuum condition and then blown down to dryness using pure nitrogen. After reaction with a mixture of N,O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine (5:1, v/v) at 70 °C for 3 hr, the derivatives were determined using a GC/MS technique below.

Gas chromatography–mass spectrometry (GC/MS) analysis of the derivatized fraction was performed using an Agilent 7890A GC coupled with an Agilent 5975C MSD. The GC separation was carried out on a DB-5MS fused silica capillary column with the GC oven temperature programmed from 50°C (2 min) to 120°C at 15°C min^{–1} and then to 300°C at 5°C min^{–1} with a final isothermal hold at 300°C for 16 min. The sample was injected in a splitless mode at an injector temperature of 280°C, and scanned from 50 to 650 Daltons using electron impact (EI) mode at 70 eV. Chemical characters and possible sources of the 20 detected organic compounds in this study were listed in Table 1, while their GC retention times and m/z ratios were shown in Fig. 2. All the detected compounds were quantified using peak area of the individual characteristic ion. In addition, GC/MS response factors of *cis*-pinonic acid, succinic acid, glutaric acid, malic acid, phthalic acids, levoglucosan and arabitol were determined using authentic

standards, while GC/MS response factors of 3-MeTHF-3,4-diols (*trans*-3-methyltetrahydrofuran-3,4-diol and *cis*-3-methyltetrahydrofuran-3,4-diol), C₅-alkene triols (*cis*-2-methyl-1,3,4-trihydroxy-1-butane, 3-methyl-2,3,4-trihydroxy-1-butane and *trans*-2-methyl-1,3,4-trihydroxy-1-butane), and 2-methyltetrols (2-methylthreitol and 2-methylerythritol) were replaced by that of erythritol, and response factors of 2-methylglyceric acid, 3-hydroxyglutaric acid, 3-methyl-1,2,3-butanetricarboxylic acid and β -caryophyllinic acid were replaced by those of glyceric acid, tartaric acid, suberic acid and *cis*-pinic acid, respectively, because the authentic standards are not commercially available. Average recoveries of the target compounds were better than 70%. No significant contamination (<10% of those in the samples) was found in the blanks. Data presented were corrected for the field blanks but not corrected for the recoveries.

OC and EC in the PM₁₀ samples were analyzed using DRI Model 2001 Carbon analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Chow et al., 2004). Inorganic ions including SO₄²⁻, NO₃⁻ and NH₄⁺ in PM₁₀ and size-resolved samples were analyzed using ion chromatography (Li et al., 2011; Shen et al., 2008). Particle in-situ pH (pH_{IS}) and aerosol liquid water content (LWC) were calculated by Aerosol Inorganic Model (AIM) using a SO₄²⁻-NO₃⁻-NH₄⁺-H⁺ system (AIM-II) (Clegg et al., 1998a, b) (<http://www.aim.env.uea.ac.uk/aim/aim.php>). These data were used in the current study to explore the sources and formation mechanisms of BSOA.

3. Results and discussion

3.1. Abundance of OC, EC and SOA in PM₁₀

3.1.1 Overall results

Table 2 summarizes the arithmetic mean concentrations and standard deviations of organic compounds, OC, EC and inorganic ions detected for the PM₁₀ samples. Particle mass (PM₁₀), OC and EC at Mt. Hua in summer were 43±17, 3.5±1.3 and 0.65±0.27 μg m⁻³, respectively, and

lower than those in winter (54 ± 24 , 5.9 ± 2.5 and $0.9 \pm 0.6 \mu\text{g m}^{-3}$) (Li et al., 2012a), mainly due to decreased emissions of biomass and coal burning for house heating. However, summertime meteorological conditions (e.g., higher temperature and RH) are favorable for secondary aerosol formation, resulting in higher concentrations of SO_4^{2-} and NH_4^+ (21 ± 12 and $4.3 \pm 2.5 \mu\text{g m}^{-3}$, respectively) in summer compared to those (5.8 ± 3.6 and $1.6 \pm 0.9 \mu\text{g m}^{-3}$, respectively) in winter (Li et al., 2011).

Eight compounds were determined as oxidation products of isoprene in the PM_{10} samples, which are 3-MeTHF-3,4-diols (the sum of *trans*-3-methyltetrahydrofuran-3,4-diol and *cis*-3-methyltetrahydrofuran-3,4-diol, $0.30 \pm 0.29 \text{ ng m}^{-3}$), 2-methylglyceric acid ($4.1 \pm 2.2 \text{ ng m}^{-3}$), C_5 -alkene triols (the sum of *cis*-2-methyl-1,3,4-trihydroxy-1-butane, 3-methyl-2,3,4-trihydroxy-1-butane and *trans*-2-methyl-1,3,4-trihydroxy-1-butane, $8.1 \pm 9.8 \text{ ng m}^{-3}$) and 2-methyltetrols (the sum of 2-methylthreitol and 2-methylerythritol, $8.5 \pm 6.4 \text{ ng m}^{-3}$) (Table 2 and Fig. 3) (Surratt et al., 2010; Lin et al., 2012). *cis*-Pinonic acid, 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) are the major photooxidized products of α -/ β -pinene, and their concentrations are 3.0 ± 1.4 , 2.1 ± 1.1 and $1.6 \pm 1.1 \text{ ng m}^{-3}$, respectively. β -Caryophyllinic acid, one of β -caryophyllene (a sesquiterpene) oxidation products, was also determined in this study, and its concentration was $2.2 \pm 1.2 \text{ ng m}^{-3}$. Contributions of BVOCs to secondary organic carbon (SOC) in the atmosphere of Mt. Hua were estimated using a tracer-based method reported by Kleindienst et al. (2007). Concentrations of estimated isoprene, α -/ β -pinene and β -caryophyllene derived SOC are 81 ± 53 , 29 ± 14 and $98 \pm 53 \text{ ngC m}^{-3}$, accounting for $2.7 \pm 1.0\%$, $0.8 \pm 0.2\%$ and $2.1 \pm 1.0\%$ of OC, respectively. It should be noted that the tracer-based method (Kleindienst et al., 2007) was developed under very limited experimental conditions of NO_x , aerosol acidity, and relative humidity. Thus, the estimated isoprene, α -/ β -pinene and β -caryophyllene derived SOC might be underestimated in the current study.

Succinic, glutaric and malic acids in the atmosphere are produced mainly by photochemical

reactions of unsaturated hydrocarbons and fatty acids emitted from biomass burning and coal combustion (Kawamura and Yasui, 2005; Wang et al., 2010). Concentrations ($2.2\text{--}5.8\text{ ng m}^{-3}$) of these compounds in the Mt. Hua PM_{10} samples are comparable to the BSOA tracers above. Phthalic acids are derived from photooxidation of polycyclic aromatic hydrocarbons (PAHs) (Wang et al., 2007; Simoneit et al., 2004b), and pyrolysis of plastic materials (Kawamura and Pavuluri, 2010). Their concentrations in the Mt. Hua samples are $0.16\text{--}4.9\text{ ng m}^{-3}$. Levoglucosan is a tracer of biomass burning, while arabitol is a metabolic product from pollen, spores, fungi, algae and bacteria (Simoneit et al., 2004a; Engling et al., 2009; Wang et al., 2009b; Wang et al., 2011b). Levoglucosan is lower in summer ($14\pm12\text{ ng m}^{-3}$) than in winter ($65\pm30\text{ ng m}^{-3}$), in contrast to arabitol ($5.5\pm3.5\text{ ng m}^{-3}$ in summer and $3.0\pm2.0\text{ ng m}^{-3}$ in winter), which is higher in summer (Li et al., 2012a), indicating a decreased biomass burning and an increased biogenic activity in the hot season.

3.1.2 Comparison between different air masses classified by backward trajectories analysis

72-h Backward trajectory analysis using HYSPLIT Trajectory Model showed that air masses reaching the sampling site during the campaign were from three directions: southerly, easterly and northerly (Fig. 1). Thus, all the samples were categorized into the three groups and compared for the differences in concentrations and compositions (Table 2). A *t*-test comparing the mean values of concentrations was also conducted to confirm if the differences between the different air masses were statistically significant (Table 2). Nearly all of the anthropogenic species (e.g. EC , SO_4^{2-} , NO_3^- , NH_4^+ , phthalic acids and levoglucosan) presented a *p*-value larger than 0.05, which statistically means there is no significant difference for these components between the three directions. However, most BSOA tracers presented higher concentrations for the southerly samples than those for the easterly and northerly samples with a *p*-value lower than 0.05 (Table 2), which is reasonable as plant vegetation is more abundant in the southern part of Qinling mountain.

3.1.3 Comparison of BSOA tracers with other studies

A comparison of concentration and diagnostic ratio of isoprene, α -/ β -pinene and β -caryophyllene products was shown in Table 3. In this study, aerosol samples were collected at a summit of Mt. Hua (2060 m a.s.l), where vegetation is limited and the ground surfaces are mostly rocks. Thus, BSOA tracers present the lowest concentration in Mt. Hua compared to those in other areas except Alert (82.5 °N, 62.3 °W) in the Canadian High Arctic region. All the tracers at the Alert site are 1–3 orders of magnitude lower than those in other regions.

2-Methyltetrols are the major products of isoprene (Kleindienst et al., 2006;Edney et al., 2005;Claeys et al., 2010), thus their contribution to organic carbon of airborne particles can be used to roughly compare the impact of isoprene-derived SOA relative to other OC sources. As shown in Table 3, the ratio of 2-methyltetrols-C/OC is highest in the equatorial region (Balbina, Brazil, 1.8%) (Claeys et al., 2004) and southeastern USA (0.52–7.0%) (Ding et al., 2008;Lin et al., 2013b), and lowest at the Arctic site (Alert, Canada 0.019%) (Fu et al., 2009). Isoprene derived products are abundant in the southeastern USA region especially in rural areas, where concentrations of total detected isoprene SOA tracers can reach up to 1245 ng m⁻³ and their contribution to organic matters (OM) is more than 19% (Lin et al., 2013b). The carbon contribution of 2-methyltetrols in Mt. Hua (0.11 ±0.06%) is lower than those (0.17–0.75%, Table 3) in other Chinese regions excluding Wangqingsha and Chongming, suggesting the lower impact of isoprene-derived SOA relative to other sources. The lowest ratios in Wangqingsha (0.070%) and Chongming (0.020%) are most likely resulted from the high anthropogenic OC input since both sites are close to the urban areas.

MBTCA is one of aged products from gas-phase oxidation of *cis*-pinonic acid (PA) by OH radical (Szmigielski et al., 2007;Henry and Donahue, 2012). Thus the ratio of MBTCA/PA ($R_{MBTCA/PA}$) is indicative of aerosol ageing (Kulmala et al., 2011). The ratios (0.54 and 1.0, Table 3) at Mt. Hua and Mt. Tai are higher than that (0.32, Table 3) at Wangqingsha, a lowland rural

site in southern China, indicating the mountain aerosols are more oxidized. Such a phenomenon may be related to the stronger mountaintop radiation that causes the BSOA being highly oxidized. Averaged ratios of MBTCA/PA in Mt. Hua were 0.71 ± 0.27 , 0.43 ± 0.31 and 0.29 ± 0.12 for the southerly, easterly and northerly samples, respectively, indicating that aerosols derived from the southerly air masses were more aged. The Mexico Campaign reported that MBTCA/PA (4.8, Table 3) in the rural area is nearly 5 times higher than that (0.91) in urban region due to more aged BSOA (Stone et al., 2010), which is consistent with the larger contributions ($25 \pm 5\%$) of aged low-MW acids (mainly oxalic acid) to WSOC at the peripheral rural site than that at urban site ($8.2 \pm 3.4\%$) (Stone et al., 2010). Concentration of MBTCA at the Arctic site is almost one order of magnitude higher than PA ($R_{MBTCA/PA} = 9.4$ at Alert, Table 3). Such a spatial variation in the ratios demonstrates a continuous oxidation of BSOA during transport.

3.2 In-situ pH and liquid water content of particles

Chemical reactions in aerosol phase or gas-particle distributions in aerosol surface are much linked to the actual pH (i.e., in-situ pH, pH_{IS}) in the aqueous phase and liquid water content (LWC) of particles (Xue et al., 2011). Thus, aerosol pH_{IS} and LWC were calculated in this study using the following equation:

$$pH_{IS} = -\log \alpha_{H^+} = -\log(\gamma_{H^+} \times n_{H^+} \times 1000/V_a) \quad (1)$$

Where α_{H^+} is activity of H^+ in mol L^{-1} in the aqueous phase on the particle, γ_{H^+} is the activity coefficient of H^+ , n_{H^+} is free H^+ in the unit of mol m^{-3} of air, and V_a is volume concentration of the aqueous phase of aerosol in ambient atmosphere in the unit of $\text{cm}^3 \text{ m}^{-3}$. γ_{H^+} , n_{H^+} and V_a as well as LWC ($\mu\text{mol m}^{-3}$) are derived using Aerosol Inorganic Model (AIM) (Clegg et al., 1998b, a). As SO_4^{2-} , NO_3^- and NH_4^+ are detected in this study, we chose AIM-II model for calculation, which considers a SO_4^{2-} - NO_3^- - NH_4^+ - H^+ system and allows variable temperature and relative humidity. As shown in Table 2, pH_{IS} are -0.08 ± 0.64 in PM_{10} at Mt. Hua, which is comparable with those in $\text{PM}_{2.5}$ samples in Hong Kong (-0.08 ± 0.81 during the summer of 2009) (Xue et al.,

2011) but higher than those of PM_{2.5} at Qinghai Lake (-1.20 ± 0.32 during the summer of 2010) (Li et al., 2013), a highland site with a distance of around 1000 km west to Mt. Hua. Total concentration of other cations (i.e., Ca²⁺, Mg²⁺, Na⁺ and K⁺) is about $1.0 \mu\text{g m}^{-3}$ and not included by the model. Thus, the in-situ pH of the Mt. Hua samples might be overestimated, although the mineral ions are much less abundant than NH₄⁺ ($4.3 \pm 2.5 \mu\text{g m}^{-3}$) (Table 2). LWC ($0.93 \pm 0.34 \mu\text{mol m}^{-3}$, Table 2) of the particles from the northerly air masses is 5–8 times lower than those from the southerly and easterly air masses, which is probably related to the differences in relative humidity of the air masses and hygroscopicity of the particles.

3.3 Effects of temperature on BSOA concentration

Temporal variations of BSOA tracers, OC and EC in PM₁₀ and meteorological conditions are shown in Fig. 3. The sharp declines of their concentrations during the rainy days possibly suggest a significant scavenging effect of wet deposition. The variations of the twelve BSOA tracers exhibit a same pattern, because they are formed via similar pathways.

The PM₁₀ samples collected during the three different groups of air masses were explored for the correlations of BSOA with meteorological parameters (Fig. 4a–u), and the statistical results of the correlations are shown in Table S1. Nearly all of the detected BSOA tracers showed a robust linear relation with ambient temperature, largely due to enhancements in BVOCs emission and BSOA production under higher temperature. Such a temperature dependence is also observed in other areas such as the central Pearl River Delta region, southern China (except 2-methylglyceric acid) (Ding et al., 2011) and Research Triangle Park, North Carolina, USA (Offenberg et al., 2011). The slopes of 2-methyltetrols in this study are 2.7, 2.0 and 0.79 for the PM₁₀ samples from southerly, easterly and northerly air masses, respectively, much lower than that (5.27) (Ding et al., 2011) in southern China. This can be explained by a higher isoprene emission due to more abundant vegetation in the south lowland region (Guenther et al., 2006).

3.4 Effects of relative humidity on BSOA concentration

As far as we know, field observations of the influence of relative humidity (RH) on SOA formation from biogenic VOCs were sparsely documented. Some chamber studies explored the effects of humidity on BSOA production. For example, Zhang et al. (2011) conducted a chamber study and found that 2-methylglyceric acid and its corresponding oligomers were enhanced in the particle-phase under lower RH condition. In contrast, 2-methyltetrols did not substantially vary under different RH conditions. However, in this study we found that concentrations of all of the detected BSOA showed a significant negative linear correlation with relative humidity (Fig. 4h-n).

In fact, an enhancing effect of aerosol acidity on BSOA formation was found by several chamber and field studies (Ding et al., 2011; Iinuma et al., 2004; Offenberg et al., 2009). Surratt et al. (2010) found that isoprene epoxydiols (IEPOX) are key intermediates of SOA formation from isoprene under low- NO_x conditions, which are initially formed in the gas-phase and subsequently partitioned into aerosol aqueous-phase. The aerosol phase IEPOX further convert to 2-methyltetrols and C_5 -alkene triols by an acid-catalyzed ring opening of this epoxydiol and a subsequent nucleophilic addition. Lin et al. (2012) again confirmed that IEPOX reactively uptake onto acidified sulfate aerosols to produce 2-methylthreitol and 2-methylerythritol as well as other IEPOX-derived SOA tracers, including C_5 -alkene triols, 3-methyltetrahydrofuran-3,4-diols, dimers, and organosulfates. Aerosol in-situ acidity is strongly dependent on relative humidity. Based on the AIM model calculations, we found that relative humidity (RH) of the mountaintop atmosphere exhibits a robust linear correlation with the in-situ pH (pH_{IS}) of the PM_{10} particles ($R=0.97$, $p<0.05$) and a moderate correlation with LWC of the particles ($R=0.80$, $p<0.05$). As shown in Fig. 4o–q, concentrations of all the calculated SOC in the air masses showed a negative linear correlation with pH_{IS} , and the correlation was even stronger when the data of rainy days were excluded (Fig. 4r), which suggests that the suppressing effect of RH on BSOA formation is

most likely related to reducing aerosol acidity. Similar studies have been performed in southeastern USA, although the AIM model for most samples didn't work due to the aerosol either being fully neutralized or the RH being too low in the region (Lin et al., 2013b; Budisulistiorini et al., 2013). Interestingly, Budisulistiorini et al. (2013) found that the IEPOX-OA factor obtained by PMF (positive matrix factorization) analysis of ACSM (Aerosol Chemical Speciation Monitor) data also showed a moderate correlation ($R=0.5$) with in situ acidity of particles.

Moreover, Zhang et al. (2011) reported that low RH circumstance can improve isoprene-derived SOA yields by promoting particle phase organic esterification process. Nguyen et al. (2011) also pointed out that the suppression of condensation and addition reactions are the most important chemical effects of the increased RH on BSOA formation. However, we found there was no clear correlation between biogenic SOC (BSOC) concentration and liquid water content (LWC) of the particles (Fig. 4s-u). High LWC is favorable for a conversion of BSOA precursors into aqueous phase and thus enhances BSOA production. On the other hand, however, high LWC may reduce particle acidity, which is unfavorable for BSOA production. In addition, variations in RH may result in changes of BVOC emissions and thus change BSOA production. In any case, more chamber and field studies are warranted in order to understand the exact mechanism of effect of RH on BSOA formation.

Phthalic acids may be produced by the oxidation of naphthalene and other polycyclic aromatic hydrocarbons (Kawamura et al., 2005; Kawamura and Ikushima, 1993). Similar to BSOA formation, these anthropogenic SOA also showed a positive correlation with temperature ($R>0.6$). A clear correlation between RH and concentration of phthalic acids was not observed in this study ($R<0.1$). However, recent investigations indicated that the yields of SOA derived from some aromatic compounds (such as xylenes and toluene) positively correlated with the particle water content (Kamens et al., 2011; Zhou et al., 2011), suggesting an importance of LWC of

particles (RH depended) on anthropogenic SOA formation.

3.5 Size distribution

To further discuss the source and formation mechanism of the BSOA in the mountain atmosphere, detailed information of their size distribution was investigated. Table 4 shows the concentration and geometric mean diameters (GMD) of the detected organic species and inorganic ions in the fine ($<2.1\mu\text{m}$) and coarse ($>2.1\mu\text{m}$) modes, and their concentrations as a function of sizes are plotted in Fig. 5.

3-MeTHF-3,4-diols, C_5 -alkene triols and 2-methyltetrols present unimodal size distribution pattern with a peak at the size of $0.7\text{--}1.1\mu\text{m}$ (Fig.5a, c and d). As mentioned above, IEPOX are key intermediates of isoprene oxidation products of 3-MeTHF-3,4-diols, C_5 -alkene triols and 2-methyltetrols under low- NO_x conditions through heterogeneous reactions in aerosol-phase (Surratt et al., 2010; Lin et al., 2012). In contrast, 2-methylglyceric acid is formed via nucleophilic attack of water on the oxirane ring of 2-methyloxirane-2-carboxylic acid (methacrylic acid epoxide, MAE), which is produced by isoprene oxidation under high- NO_x conditions (Lin et al., 2013a). 2-Methylglyceric acid in the Mt. Hua aerosols present a bimodal size distribution pattern with a major peak in the fine mode ($<2.1\mu\text{m}$) and a minor peak in the coarse mode ($>2.1\mu\text{m}$) (Fig.5b).

cis-Pinonic acid exhibits a bimodal pattern with a large peak in the coarse mode ($>2.1\mu\text{m}$) (Fig. 5e), in contrast to 3-hydroxyglutaric acid and MBTCA, which only occur in the fine mode (Fig. 5f and g). Such distributions are consistent with those in Mainz, Germany (Zhang et al., 2010). *cis*-Pinonic acid is formed by a gas-phase oxidation of pinene with ozone and a subsequent adsorption onto pre-existing particles (Hallquist et al., 2009). On the contrary, MBTCA is likely formed in the gas phase by further reactions of *cis*-pinonic acid or *cis*-pinic acid involving participation of OH radical (Jaoui et al., 2005; Szmigielski et al., 2007). The differences in size distributions of *cis*-pinonic acid and MBTCA can be ascribed to the highly

volatile nature of *cis*-pinonic acid. Zhang et al. (2010) pointed out that *cis*-pinonic acid predominantly present in the gas phase. Coarse particle are generally basic, because they are in most cases enriched with mineral species. Therefore, *cis*-pinonic acid in gas-phase may prefer to reactively uptake onto coarse particles. Only a fine mode of β -caryophyllinic acid was observed in the mountain atmosphere (Fig. 5h).

Succinic and glutaric acids are formed mostly from anthropogenic volatile organic compounds, which are firstly oxidized as gaseous keto-carboxylic acids and then partitioned into particle phase followed by a further oxidation as dicarboxylic acids (Wang et al., 2011a), thus both present a bimodal size distribution (Fig. 5i and j). On the contrary, malic acid is found to be mostly produced in biomass combustion process and emitted into the air as fine particles (Wang et al., 2011a; Wang et al., 2012), thus malic acid showed a fine mode pattern (Fig. 5k). *o*-Phthalic acid is formed via a gaseous oxidation of naphthalene and followed by a subsequent adsorption/condensation onto pre-existing particles, thus, showed a bimodal pattern (Fig. 5l), in contrast to a unimodal pattern of *p*-phthalic acid (Fig. 5n), which is largely formed by a pyrolysis of plastic materials and emitted into the air as fine particles (Wang et al., 2012). Levoglucosan, a key tracer for biomass burning, presents a unimodal distributing, peaking at a size of 0.7–1.1 μm in summer (Fig. 5o). In contrast, arabitol is dominated in coarse particle as it mostly originates from pollen, spore and other biota (Fig. 5p). SO_4^{2-} and NH_4^+ are dominated in the fine mode (Fig. 5q and s), similar to those in winter (Li et al., 2011). However, coarse particles in the mountain atmosphere are more enriched in NO_3^- compared to that in Xi'an (unreported data), a mega-city near Mt. Hua (Fig. 5r). Such a shift to large particles is caused by an evaporation of nitrate from fine particles and a subsequent adsorption onto coarse particles during the air mass transport onto the mountaintop. Na^+ and K^+ are dominated in fine particles in the Mt. Hua region (Fig. 5t and u), suggesting they are mainly derived from biomass burning instead of soil resuspension. Ca^{2+} and Mg^{2+} are the tracers of dust emission, and thus they are abundant in coarse particles (Fig. 5v and

w).

4. Summary and conclusion

BSOA derived from isoprene, pinene and sesquiterpene were determined for PM₁₀ and size-resolved aerosols collected at the mountaintop of Mt. Hua. Backward trajectories analysis showed that nearly all the BSOA tracers present higher concentrations in the samples from the southerly than those from the easterly and northerly, indicating higher BVOC emissions and/or more BSOA production. Concentrations of the BSOA in the mountain samples increased with an increase in temperature during the campaign, because higher temperature is favorable for BVOCs emission and subsequent oxidation. In contrast, RH showed significant linear negative correlations with concentrations of all the isoprene, pinene and caryophyllene products. Based on the AIM model calculation, we found that an increase in RH can result in a decrease in particle in-situ acidity, which reduces the effect of acid-catalysis on BSOA formation. However, such a significant relation was not observed for LWC and BSOA. Size distribution details were also explored for the target compounds. Most of the BSOA are enriched in the fine mode (<2.1 μm) except for *cis*-pinonic acid, which is dominated in the coarse mode (>2.1 μm) due to its highly volatile nature. Size distributions of levoglucosan, arabitol and other secondary aerosols were also investigated. These size distribution details are helpful for recognizing their atmospheric fate including formation, adsorption and evaporation.

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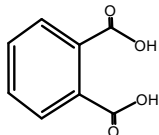
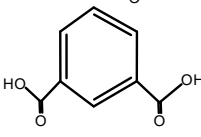
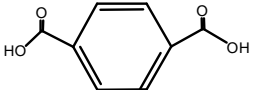
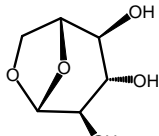
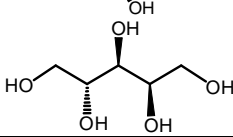
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626Table 1
Chemical characters and possible sources of detected organic tracers.

Organic marker	Chemical structure	Molecular formula	Molecular weight	m/z ^a	Possible source
I. Isoprene derived SOA					
<i>trans</i> -3-Methyltetrahydrofuran-3,4-diol		C ₅ H ₁₀ O ₃	118	262	
<i>cis</i> -3-Methyltetrahydrofuran-3,4-diol		C ₅ H ₁₀ O ₃	118	262	
2-Methylglyceric acid		C ₄ H ₈ O ₄	120	103	
<i>cis</i> -2-Methyl-1,3,4-trihydroxy-1-butene		C ₅ H ₁₀ O ₃	118	231	Photochemical product of isoprene (Lin et al., 2012; Surratt et al., 2010).
3-Methyl-2,3,4-trihydroxy-1-butene		C ₅ H ₁₀ O ₃	118	231	
<i>trans</i> -2-Methyl-1,3,4-trihydroxy-1-butene		C ₅ H ₁₀ O ₃	118	231	
2-Methylthreitol		C ₅ H ₁₂ O ₄	136	147	
2-Methylerythritol		C ₅ H ₁₂ O ₄	136	147	
II. α -/ β -pinene derived SOA					
<i>cis</i> -Pinonic acid		C ₁₀ H ₁₆ O ₃	184	171	
3-Hydroxyglutaric acid		C ₅ H ₈ O ₅	148	147	Photochemical product of monoterpene (Eddingsaas et al., 2012).
3-Methyl-1,2,3-butanetricarboxylic acid (MBTCA)		C ₈ H ₁₂ O ₆	204	147	
III. β -caryophyllene derived SOA					
β -Caryophyllinic acid		C ₁₄ H ₂₂ O ₄	254	383	Photochemical product of β -caryophyllene (Fu et al., 2009).
IV. Other organic compounds					
Succinic acid		C ₄ H ₆ O ₄	118	247	
Glutaric acid		C ₅ H ₈ O ₄	132	147	Photochemical product of unsaturated hydrocarbons and fatty acids; direct emission from coal and biomass burning (Kawamura et al., 2005).
Malic acid		C ₄ H ₆ O ₅	134	147	

<i>o</i> -Phthalic acid		$C_8H_6O_4$	166	295	Photochemical product of toluene, xylene, naphthalene and other anthropogenic pollutants (Kawamura et al., 2005).
<i>m</i> -Phthalic acid		$C_8H_6O_4$	166	295	
<i>p</i> -Phthalic acid		$C_8H_6O_4$	166	295	
Levoglucosan		$C_6H_{10}O_5$	162	217	Pyrolysis product of materials containing cellulose (Simoneit et al., 2004a; Li et al., 2012b).
Arabitol		$C_5H_{12}O_5$	152	217	Direct emission by microorganism, plants and animals (Li et al., 2012b; Simoneit et al., 2004a).

^a Mass-to-charge ratio of fragment ions for qualification and quantification.

Table 2
Concentrations (arithmetic mean \pm standard deviation, ng m⁻³) and *t*-test results of the BSOA tracers and other compounds in the PM₁₀ samples in Mt. Hua from southerly (S), easterly (E) and northerly (N) air masses.

	Concentration				<i>p</i> -value (<i>t</i> -test)		
	S (N=17)	E (N=11)	N (N=6)	Mean(N=34)	S-E	S-N	E-N
I. Inorganic ions							
T (°C)	18 \pm 2.1	16 \pm 1.1	18 \pm 2.2	17 \pm 2.1	0.002	0.230	0.372
RH (%)	85 \pm 10	91 \pm 5.0	64 \pm 3	84 \pm 3	0.036	0.022	0.032
PM ₁₀ (μg m ⁻³)	42 \pm 17	42 \pm 17	46 \pm 6.6	43 \pm 17	0.664	0.808	0.609
OC (μg m ⁻³)	4.0 \pm 1.2	3.0 \pm 1.2	3.0 \pm 0.87	3.5 \pm 1.3	0.019	0.127	0.612
EC (μg m ⁻³)	0.65 \pm 0.26	0.57 \pm 0.20	0.78 \pm 0.37	0.65 \pm 0.27	0.790	0.567	0.746
SO ₄ ²⁻ (μg m ⁻³)	19 \pm 9.9	23 \pm 11	15 \pm 6.8	21 \pm 12	0.141	0.191	0.066
NO ₃ ⁻ (μg m ⁻³)	1.2 \pm 1.7	1.5 \pm 1.3	2.0 \pm 0.4	1.4 \pm 1.4	0.617	0.415	0.603
NH ₄ ⁺ (μg m ⁻³)	4.0 \pm 2.0	5.1 \pm 2.5	3.1 \pm 1.4	4.3 \pm 2.5	0.079	0.175	0.046
Na ⁺ (μg m ⁻³)	0.23 \pm 0.06	0.30 \pm 0.13	0.23 \pm 0.08	0.23 \pm 0.07	0.353	0.990	0.546
K ⁺ (μg m ⁻³)	0.28 \pm 0.13	0.28 \pm 0.15	0.20 \pm 0.12	0.27 \pm 0.14	0.079	0.175	0.046
Mg ²⁺ (μg m ⁻³)	0.10 \pm 0.05	0.07 \pm 0.03	0.15 \pm 0.06	0.10 \pm 0.05	0.903	0.229	0.279
Ca ²⁺ (μg m ⁻³)	0.40 \pm 0.27	0.28 \pm 0.11	0.70 \pm 0.27	0.41 \pm 0.27	0.211	0.028	0.002
pH _{IS} ^a	0.0 \pm 0.55	0.30 \pm 0.39	-1.08 \pm 0.47	-0.08 \pm 0.64	0.145	0.032	0.001
LWC ^a (μmol m ⁻³)	4.85 \pm 5.27	7.01 \pm 4.51	0.93 \pm 0.34	4.87 \pm 4.90	0.197	0.113	0.001
II. Isoprene derived SOA							
3-MeTHF-3,4-diols ^b	0.43 \pm 0.29	0.16 \pm 0.12	0.13 \pm 0.08	0.30 \pm 0.29	0.002	0.001	0.438
2-methylglyceric acid	4.7 \pm 1.7	3.9 \pm 2.4	2.7 \pm 1.7	4.1 \pm 2.2	0.139	0.009	0.307
C ₅ -alkene triols ^b	12 \pm 12	3.9 \pm 3.1	7.7 \pm 8.7	8.1 \pm 9.8	0.019	0.359	0.375
2-methyltetrols ^b	12 \pm 6.3	6.1 \pm 4.8	4.1 \pm 3.1	8.5 \pm 6.4	0.012	0.001	0.341
subtotal	29 \pm 19	14 \pm 10	15 \pm 13	21 \pm 17	0.018	0.065	0.897
SOC _{isoprene} (ngC m ⁻³) ^c	106 \pm 49	65 \pm 45	44 \pm 30	81 \pm 53	0.017	0.005	0.313
III. α -/ β -pinene derived SOA							
<i>cis</i> -pinonic acid	3.3 \pm 1.4	2.5 \pm 1.1	3.1 \pm 1.4	3.0 \pm 1.4	0.083	0.387	0.656
3-hydroxyglutaric acid	2.6 \pm 1.1	1.6 \pm 0.78	1.4 \pm 0.67	2.1 \pm 1.1	0.009	0.008	0.371
MBTCA	2.2 \pm 1.1	1.0 \pm 0.64	0.88 \pm 0.49	1.6 \pm 1.1	0.001	0.004	0.537
subtotal	8.1 \pm 3.1	5.1 \pm 2.3	5.3 \pm 2.4	6.6 \pm 3.3	0.006	0.024	0.837
SOC _{pinene} (ngC m ⁻³) ^c	35 \pm 13	22 \pm 9.8	23 \pm 10	29 \pm 14	0.006	0.024	0.837
IV. β -caryophyllene derived SOA							
β -caryophyllinic acid	2.7 \pm 1.1	1.9 \pm 1.0	2.3 \pm 1.6	2.2 \pm 1.2	0.056	0.255	0.903
SOC _{caryophyllene} (ngC m ⁻³) ^c	116 \pm 47	81 \pm 42	98 \pm 72	98 \pm 53	0.056	0.255	0.903
V. Other organic compounds							
Succinic acid	6.7 \pm 3.1	6.8 \pm 3.5	1.6 \pm 0.41	5.8 \pm 3.6	0.716	0.001	0.002
Glutaric acid	2.4 \pm 1.0	2.2 \pm 1.3	0.88 \pm 0.31	2.2 \pm 1.5	0.295	0.007	0.013
Malic acid	7.3 \pm 2.4	5.1 \pm 2.6	2.7 \pm 1.5	5.8 \pm 3.2	0.015	0.001	0.062
<i>o</i> -Phthalic acid	6.2 \pm 2.3	4.4 \pm 2.1	2.9 \pm 1.5	4.9 \pm 2.5	0.026	0.002	0.165
<i>m</i> -Phthalic acid	0.18 \pm 0.08	0.13 \pm 0.06	0.15 \pm 0.08	0.16 \pm 0.08	0.095	0.262	0.922
<i>p</i> -Phthalic acid	2.7 \pm 2.2	1.7 \pm 1.7	3.0 \pm 3.0	2.3 \pm 2.2	0.189	0.915	0.439
Levoglucosan	17 \pm 13	12 \pm 12	14 \pm 6.8	14 \pm 12	0.306	0.479	0.853
Arabitol	6.1 \pm 4.0	4.3 \pm 2.8	5.9 \pm 0.63	5.5 \pm 3.5	0.494	0.645	0.894

^apH_{IS} and LWC: in-situ pH and liquid water content in the aqueous phase of PM₁₀, both are calculated based on AIM (Aerosol Inorganic Model). ^b3-MeTHF-3,4-diols: *trans*-3-methyltetrahydrofuran-3,4-diol+*cis*-3-methyltetrahydrofuran-3,4-diol; C₅-alkene triols: *cis*-2-methyl-1,3,4-trihydroxy-1-butane+3-methyl-2,3,4-trihydroxy-1-butane+*trans*-2-methyl-1,3,4-trihydroxy-1-butane; 2-methyltetrols: 2-methylthreitol+2-methylerythritol. ^cTotal mass concentrations of SOC (secondary organic carbon) produced by isoprene, α -/ β -pinene, and β -caryophyllene were calculated using a tracer-based method reported by Kleindienst et al. (2007).

638 Table 3
639 Concentrations (ng m⁻³) of BSOA in Mt. Hua and other regions in the world during summer.

Location	Latitude (°)	Aerosols type	Isoprene products	α -/ β -pinene products	β -caryophyllene products	2-methyltetrols -C/OC (%)	R _{MBTCA/PA}	Reference
Changbai, China	42°24'N	PM _{2.5}	53	31	NA ^a	0.45	NA	(Wang et al., 2008)
Mt. Tai, China	36°41'N	TSP	171	30	12	0.32	1.0	(Fu et al., 2010)
Mt. Hua, China	34°29'N	PM ₁₀	13	6.6	2.2	0.11	0.54	This study
Chongming, China	30°50'N	PM _{2.5}	48	1.8	NA	0.02	NA	(Wang et al., 2008)
Dinghu, China	23°10'N	PM _{2.5}	26	NA	NA	0.17	NA	(Wang et al., 2008)
Wangqingsha, China	22°42'N	PM _{2.5}	31	6.6	0.54	0.07	0.32	(Ding et al., 2011)
Hong Kong, China	22°13'N	PM _{2.5}	30	198	13	0.24	NA	(Hu et al., 2008)
Hainan, China	18°40'N	PM _{2.5}	51	9.4	NA	0.75	NA	(Wang et al., 2008)
Alert, Canada	82°30'N	TSP	0.30	1.6	0.12	0.02	9.4	(Fu et al., 2009)
Hyytiälä, Finland	61°51'N	PM ₁	17	65	NA	0.25	NA	(Kourtchev et al., 2008a)
Jülich, Germany	50°54'N	PM _{2.5}	21	26	NA	0.14	NA	(Kourtchev et al., 2008b)
RTP, NC, USA	35°54'N	PM _{2.5}	137	153	11	NA	NA	(Lewandowski et al., 2007)
S.E. USA	30°26'N- 33°56'N	PM _{2.5}	40-1245	NA	NA	0.52-7.0	NA	(Lin et al., 2013b; Ding et al., 2008)
An urban site in Mexico	19°29'N	PM _{2.5}	34	48	3.4	0.17	0.91	(Stone et al., 2010)
A rural site in Mexico	19°42'N	PM _{2.5}	32	55	5.7	0.28	4.8	(Stone et al., 2010)
Balbina, Brazil	1°55'S	PM _{2.5}	57	NA	NA	1.8	NA	(Claeys et al., 2004)

640 ^a NA: not available.

Table 4
Concentration (ng m⁻³) and geometric mean diameters (GMD, μm) of BSOA and other components in
fine (<2.1 μm) and coarse modes (>2.1 μm)

	Fine mode (<2.1 μm)		Coarse mode (>2.1 μm)	
	Concentration	GMD ^a	Concentration	GMD ^a
Particle mass (μg m ⁻³)	26±3.7	0.82±0.01	20±3.9	9.82±1.27
SO ₄ ²⁻ (μg m ⁻³)	11±1.4	0.89±0.03	3.0±0.18	10.0±1.51
NO ₃ ⁻ (μg m ⁻³)	0.81±0.45	0.58±0.17	1.2±0.32	9.41±2.06
NH ₄ ⁺ (μg m ⁻³)	2.4±0.51	0.90±0.04	0.04±0.01	5.97±2.01
Na ⁺ (μg m ⁻³)	0.25±0.01	0.80±0.03	0.09±0.02	3.63±0.04
K ⁺ (μg m ⁻³)	0.13±0.03	0.91±0.04	0.02±0.01	10.1±3.25
Mg ²⁺ (μg m ⁻³)	0.08±0.01	0.89±0.05	0.08±0.02	5.75±0.41
Ca ²⁺ (μg m ⁻³)	0.25±0.07	0.89±0.03	0.36±0.21	7.95±1.12
I. Isoprene derived SOA				
3-MeTHF-3,4-diols	0.28±0.03	0.78±0.04	0.05±0.01	6.82±1.69
2-methylglyceric acid	2.3±0.54	0.87±0.01	1.3±0.27	8.77±2.68
C ₅ -alkene triols	9.2±2.6	0.84±0.03	0.98±0.22	6.34±1.62
2-methyltetrols	10±1.2	0.81±0.04	3.2±0.9	6.63±1.67
II. α-/β-pinene derived SOA				
cis-pinonic acid	1.6±0.57	0.74±0.03	2.4±0.81	8.40±2.81
3-hydroxyglutaric acid	1.6±0.32	0.77±0.02	ND ^b	ND ^b
MBTCA	1.5±0.30	0.80±0.04	0.05±0.01	2.70±0.00
III. β-caryophyllene derived SOA				
β-caryophyllinic acid	1.2±0.10	0.79±0.01	ND ^b	ND ^b
III. Other organic compounds				
Succinic acid	4.9±0.97	0.98±0.02	12.0±0.54	9.96±2.76
Glutaric acid	1.5±0.11	0.88±0.04	0.62±0.17	9.22±2.93
Malic acid	5.5±0.95	0.82±0.04	0.47±0.15	9.12±3.70
o-Phthalic acid	4.6±0.87	0.76±0.03	4.3±1.8	9.76±3.11
m-Phthalic acid	0.11±0.01	0.73±0.04	0.04±0.01	8.97±3.19
p-Phthalic acid	1.8±0.44	0.72±0.06	0.38±0.22	9.52±5.94
Levoglucosan	11±1.1	0.63±0.05	1.3±0.11	6.83±2.28
Arabitol	0.32±0.06	0.68±0.08	7.1±1.34	8.21±2.78

^a logGMD = (ΣC_i logDp_i) / ΣC_i, where C_i is the concentration of compound in size *i* and Dp_i is the geometric mean particle diameter collected on stage *i* (Hinds, 1999).

^b ND: not detected.

Figure Caption

Fig. 1. Location of the sampling site (Mt. Hua; 34° 29' N, 110° 05' E; 2060 m a.s.l.) and 72-h backward air mass trajectories reaching the summit during the sampling in the summer of 2009.

Fig. 2. GC/MS ion chromatography obtained for a trimethylsilylated PM₁₀ sample collected on 2009-8-15 (1. *trans*-3-methyltetrahydrofuran-3,4-diol; 2. *cis*-3-methyltetrahydrofuran-3,4-diol; 3. succinic acid; 4. 2-methylglyceric acid; 5. *cis*-2-methyl-1,3,4-trihydroxy-1-butane; 6. 3-methyl-2,3,4-trihydroxy-1-butane; 7. *trans*-2-methyl-1,3,4-trihydroxy-1-butane; 8. glutaric acid; 9. malic acid; 10. *cis*-pinonic acid; 11. 2-methylthreitol; 12. 2-methylerythritol; 13. 3-hydroxyglutaric acid; 14. *o*-phthalic acid; 15. levoglucosan; 16. arabinol; 17. 3-methyl-1,2,3-butanetricarboxylic acid; 18. *m*-phthalic acid; 19. *p*-phthalic acid; 20. β -caryophyllinic acid).

Fig. 3. Temporal variations of biogenic products, temperature, relative humidity, pH_{IS} (in-situ acidity of particles), LWC (liquid water content of particles), OC and EC (organic and elemental carbon). The shadows denote rainy periods. 3-MeTHF-3,4-diols: the sum of *trans*-3-methyltetrahydrofuran-3,4-diol and *cis*-3-methyltetrahydrofuran-3,4-diol; MBTCA: 2-methyl-1,2,3-butanetricarboxylic acid.

Fig. 4. Linear fit regressions of (a–g) BSOA tracers with temperature, (h–n) BSOA with relative humidity, (o–r) BSOC with in-situ pH (pH_{IS}), and (s–u) BSOC with liquid water content (LWC). S, E, N: PM₁₀ aerosols from southerly (S), easterly (E) and northerly (N) air masses, respectively. MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid. SOC_{isoprene}, SOC_{pinene} and SOC_{caryophellene}: the total mass concentrations of SOC (secondary organic carbon) produced by isoprene, α - β -pinene, and β -caryophyllene were calculated using a tracer-based method reported by Kleindienst et al. (2007). Fig. 4r excludes the samples collected on rainy days. All the values presented here are daily averages.

Fig. 5. Size distributions of (a–h) BSOA tracers, (i–p) other organic compounds, (q–w) inorganic ions, and (x) particle mass (3-MeTHF-3,4-diols: the sum of *trans*-3-methyltetrahydrofuran-3,4-diol and *cis*-3-methyltetrahydrofuran-3,4-diol; MBTCA: 2-methyl-1,2,3-butanetricarboxylic acid).

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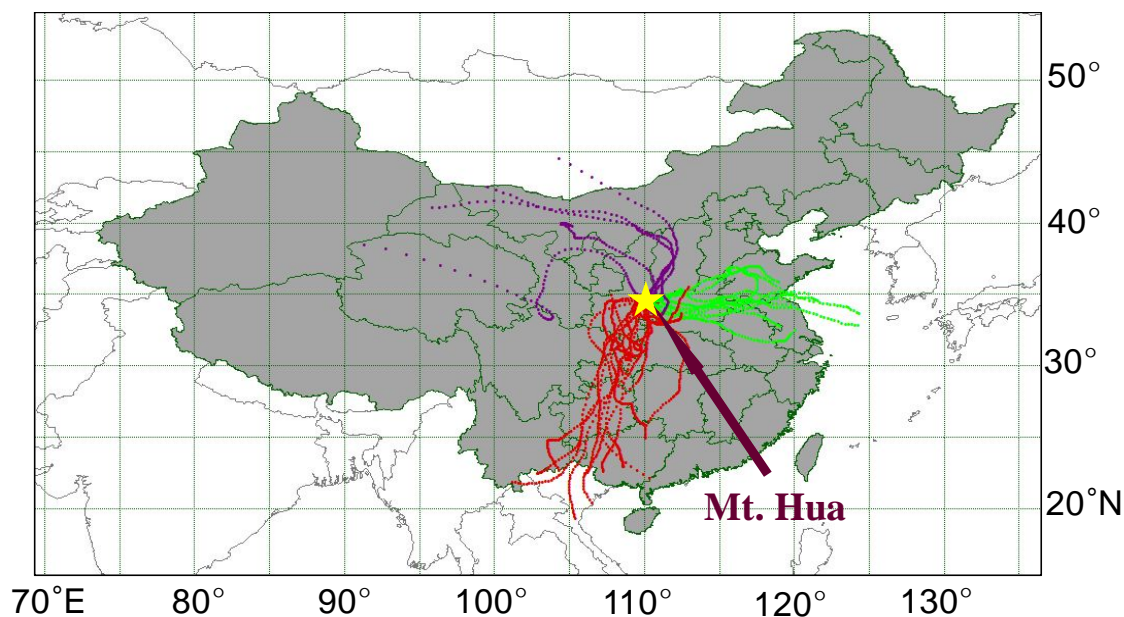


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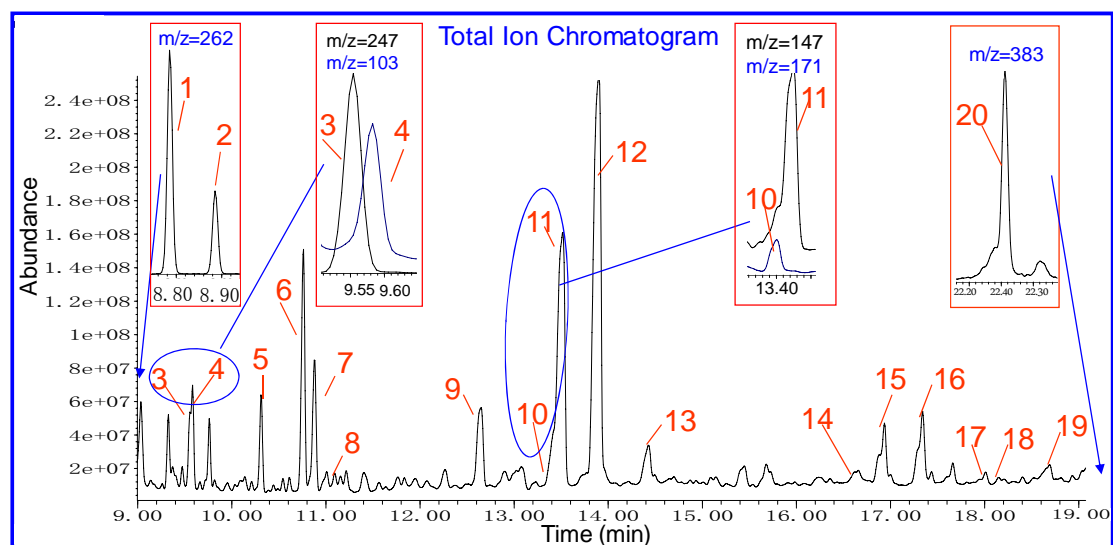


Fig. 2. GC/MS ion chromatography obtained for a trimethylsilylated PM₁₀ sample collected on 2009-8-15 (1. *trans*-3-methyltetrahydrofuran-3,4-diol; 2. *cis*-3-methyltetrahydrofuran-3,4-diol; 3. succinic acid; 4. 2-methylglyceric acid; 5. *cis*-2-methyl-1,3,4-trihydroxy-1-butane; 6. 3-methyl-2,3,4-trihydroxy-1-butane; 7. *trans*-2-methyl-1,3,4-trihydroxy-1-butane; 8. glutaric acid; 9. malic acid; 10. *cis*-pinonic acid; 11. 2-methylthreitol; 12. 2-methylerythritol; 13. 3-hydroxyglutaric acid; 14. *o*-phthalic acid; 15. levoglucosan; 16. arabinol; 17. 3-methyl-1,2,3-butanetricarboxylic acid; 18. *m*-phthalic acid; 19. *p*-phthalic acid; 20. β -caryophyllinic acid).

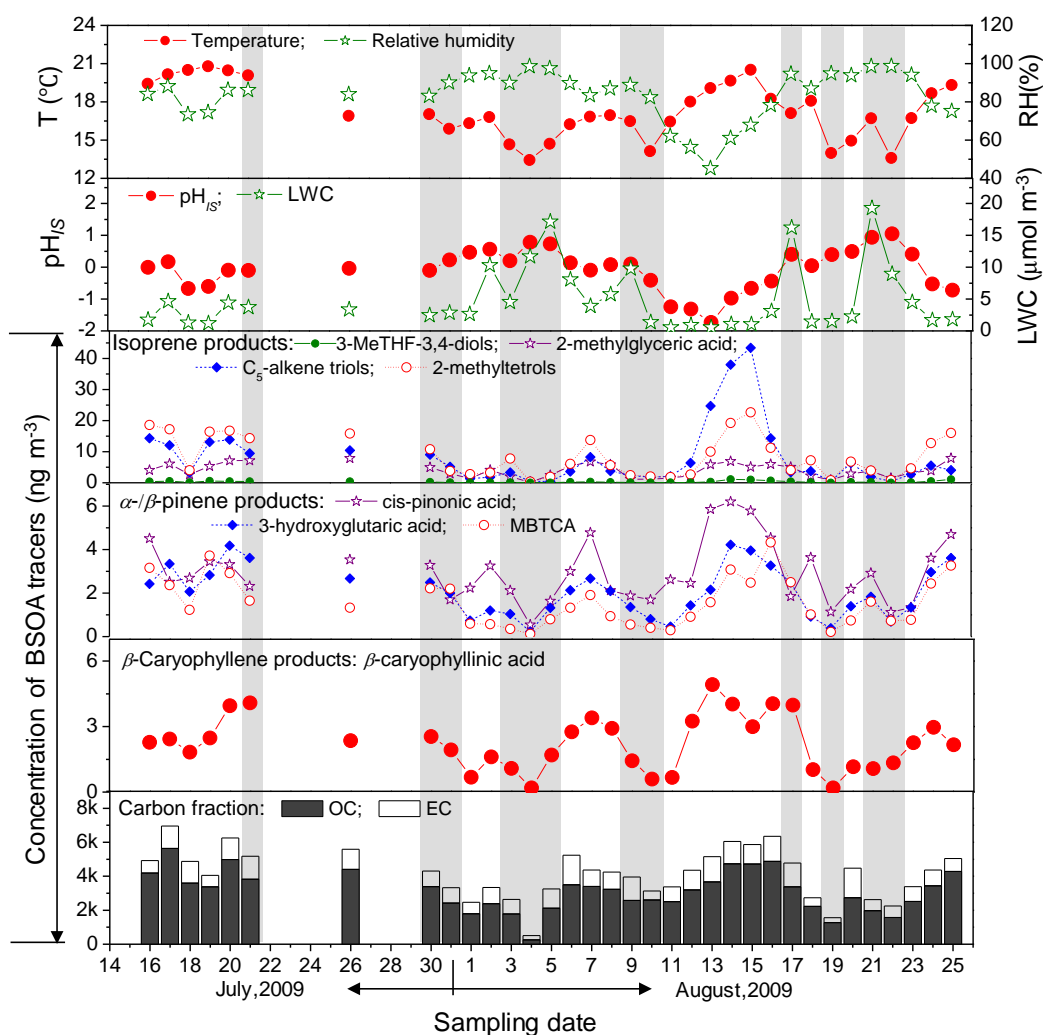


Fig. 3. Temporal variation of biogenic products as well as temperature, relative humidity, pH_{IS} (in-situ acidity of particles), LWC (liquid water content of particles), OC and EC (organic and elemental carbon). The shadows denote rainy periods. 3-MeTHF-3,4-diols: 3-methyltetrahydrofuran-3,4-diols; MBTCA: 2-methyl-1,2,3-butanetricarboxylic acid.

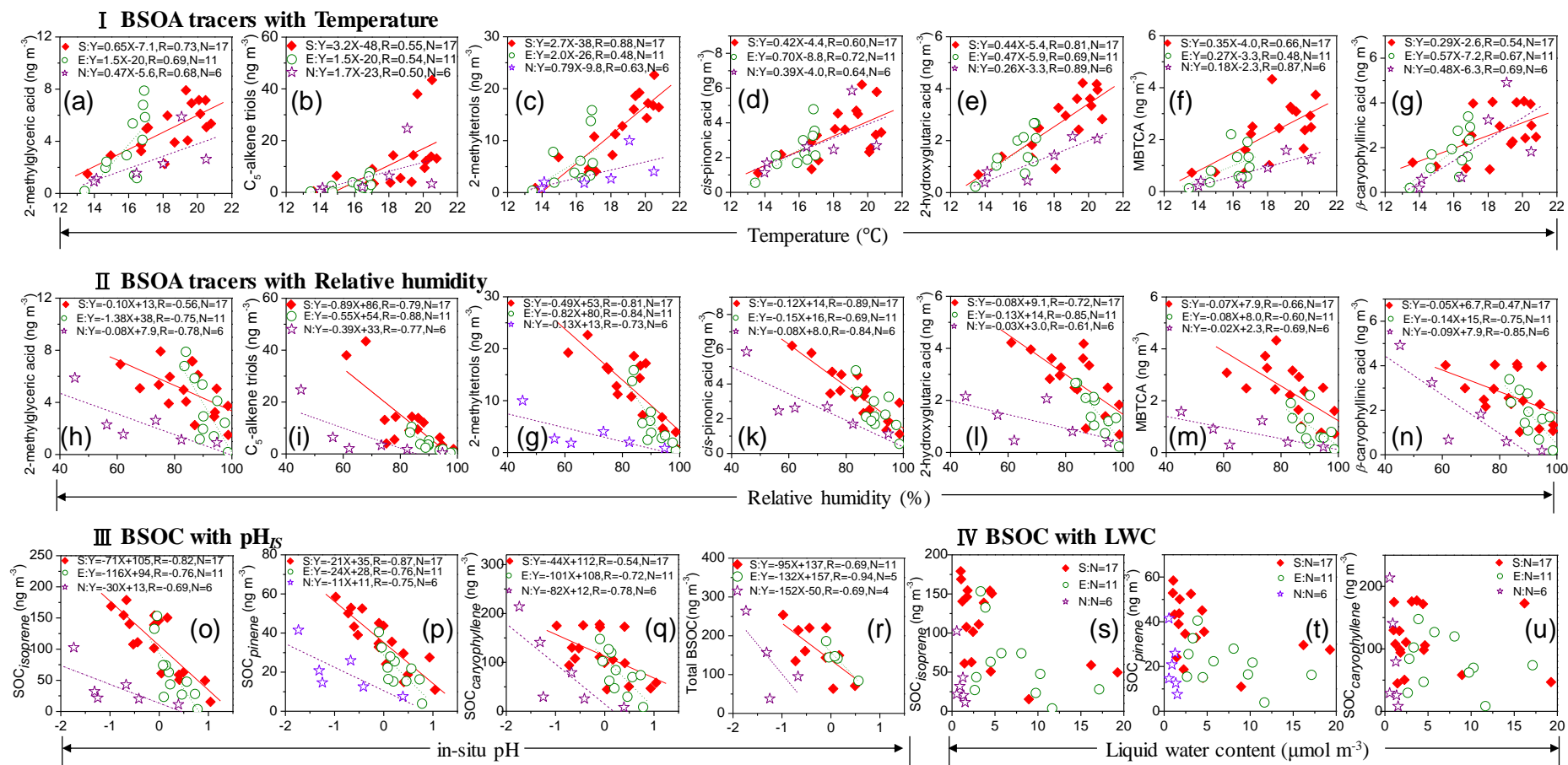


Fig. 4. Linear fit regressions of (a–g) BSOA tracers with temperature, (h–n) BSOA with relative humidity, (o–r) BSOC with in-situ pH (pH_S), and (s–u) BSOC with liquid water content (LWC). S, E, N: PM₁₀ aerosols from southerly (S), easterly (E) and northerly (N) air masses, respectively. MBTCA: 3-methyl-1,2,3-butanetricarboxylic acid. SOC_{isoprene}, SOC_{pinene} and SOC_{caryophyllene}: the total mass concentrations of SOC (secondary organic carbon) produced by isoprene, α -/ β -pinene, and β -caryophyllene were calculated using a tracer-based method reported by Kleindienst et al. (2007). Fig. 4r excludes the samples collected on rainy days. All the values presented here are daily averages.

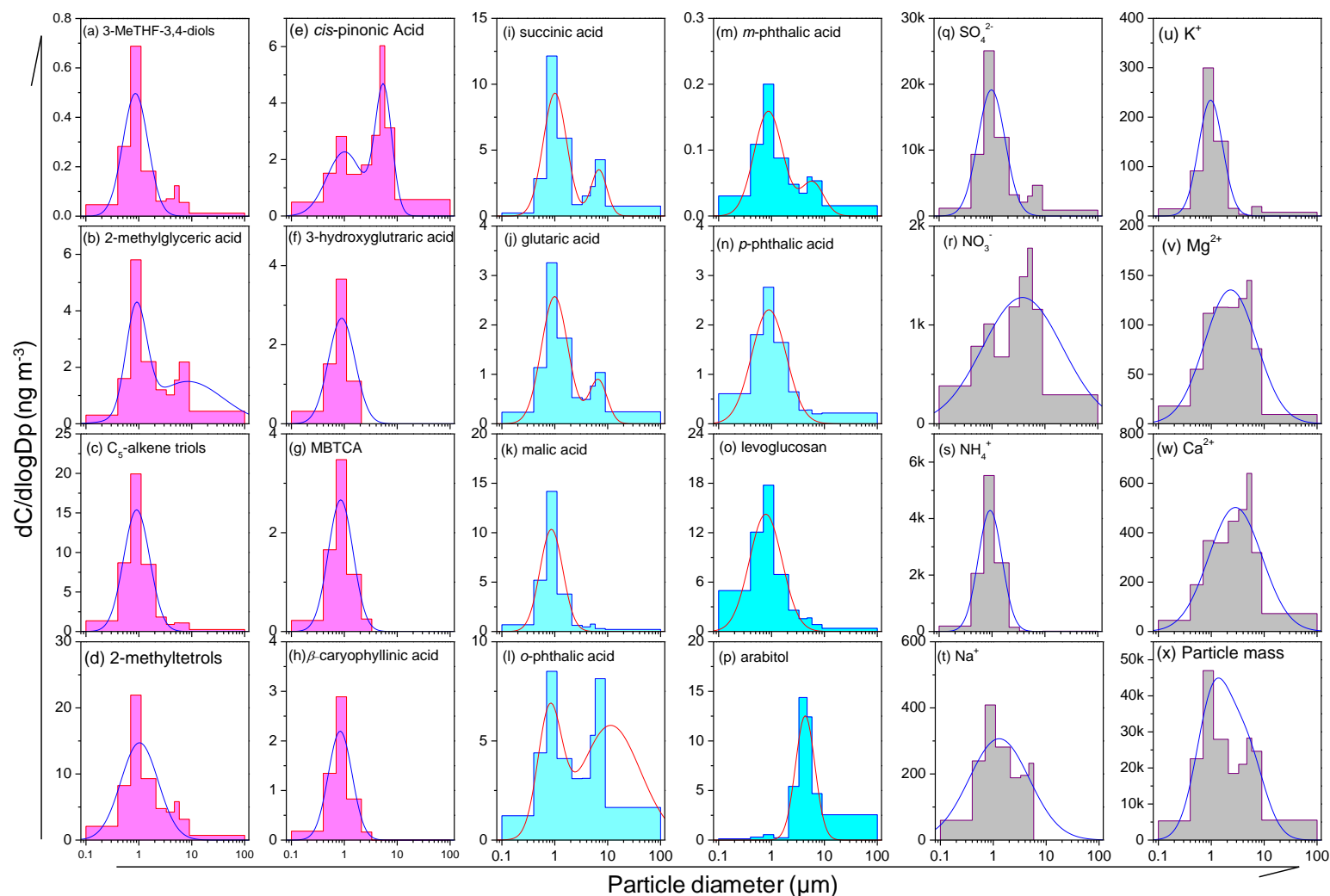


Fig. 5. Size distribution of (a-h) BSOA tracers, (i-p) other organic compounds, (q-w) inorganic ions, and (x) particle mass (3-MeTHF-3,4-diols: 3-methyltetrahydrofuran-3,4-diols; MBTCA: 2-methyl-1,2,3-butanetricarboxylic acid).